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 (72) Inventors GÜNTHER GIESSELMANN
 GERD SCHREYER and
 RUDOLF WAGNER



(54) A PROCESS FOR THE PRODUCTION OF HYDROGEN PEROXIDE

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of hydrogen peroxide.

In the anthraquinone process (AO-process) for the production of hydrogen peroxide, a 2 - alkyl anthraquinone, dissolved in an organic water-immiscible solvent, is catalytically hydrogenated to form the corresponding 2 - alkyl anthrahydroquinone and then oxidised with air or with oxygen-enriched air, the 2 - alkyl anthraquinone used being recovered with formation of hydrogen peroxide. The hydrogen peroxide is extracted with water and the solution of the 2 - alkyl anthraquinone in the organic solvent is recycled to the hydrogenation stage.

During the successive recyclings, the 2 - alkyl anthraquinone is partly converted into the corresponding 2 - alkyl tetrahydroanthraquinone which in turn can give hydrogen peroxide through successive reduction and oxidation, i.e. also takes an active part in the circuit as reaction support.

It is known from DT-PS No. 2,018,686 (U.K. Patent Specification No. 1,354,031) that tetra - substituted ureas can be used as components of a solvent mixture with hydrocarbons in the alkyl anthraquinone process. In this way, the capacity of the working solution for the production of hydrogen peroxide is significantly increased because the above-mentioned ureas have a better solubility for alkyl anthrahydroquinones.

In addition to a high capacity, however, a working solution is required *inter alia* to have a high distribution coefficient with respect to

aqueous hydrogen peroxide in order with minimal outlay to obtain a high concentration of hydrogen peroxide in the extraction stage.

In the present context, the distribution coefficient is the quotient of the hydrogen peroxide concentrations which are obtained in the equilibrium state of a 2 - phase mixture of water-working solution in the aqueous phase

kg H₂O₂

kg of aqueous solution

and in the organic phase

kg H₂O₂

kg of working solution

The presence of a tetrasubstituted urea such as N,N - diethyl N',N' - di - n - butyl urea which allows a high capacity of the working solution to produce hydrogen peroxide, is, however, unfavourable from the point of view of the distribution coefficient.

In the process according to DT-PS No. 1,261,838, alkyl phosphoric acid esters are used in conjunction with hydrocarbons as solvents for the alkyl anthraquinone process. Although working solutions such as these afford only moderate production capacities, they are distinguished by an extremely good distribution coefficient with respect to aqueous hydrogen peroxide.

Although a very high distribution coefficient affords advantages in the extraction stage, it can also be extremely undesirable from a certain value downwards for the following reasons: in the oxidation stage of the recycle process for the production of hydrogen peroxide, the hydrogen peroxide formed inevitably undergoes decomposition to a limited extent. However, even minor disturbances in operation are sufficient to increase

70-75 vol% toluene/benzene mixture

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the decomposition rate to such an extent that an aqueous phase is formed in addition to the organic phase. If the corresponding working solution has "too good" a distribution coefficient with respect to aqueous hydrogen peroxide, aqueous hydrogen peroxide can be formed in addition to the organic phase in such a high concentration that the system as a whole demonstrably represents an explosive mixture.

Our own experiments have shown that two-phase mixtures of standard working solution with aqueous hydrogen peroxide which exceed a hydrogen peroxide content of 50% by weight can propagate detonations.

One way out of the situation described above could be to combine solvents for anthrahydroquinones in such a way that

a) the working solution's capacity for the production of hydrogen peroxide is as high as possible.

b) a distribution coefficient with respect to aqueous hydrogen peroxide is present which, in the oxidation stage, does not allow the formation of an explosive mixture, but which nevertheless is high enough to be able to produce H_2O_2 in the requisite concentration at reasonable cost.

The following working solutions are mixtures of this type: according to more of our own tests, a working solution which contains as solvent 75 parts of a hydrocarbon mixture, 12.5 parts of tris - 2 - ethylhexyl phosphate and 12.5 parts of N,N - diethyl - N',N' - di - n - butyl urea, despite 25% higher charging, i.e. 12.5 g of hydrogen peroxide per litre of working solution, only allows the enrichment of at most 47.5% by weight aqueous hydrogen peroxide in addition to the organic phase. The resulting mixture is outside the danger limit.

For a hydrogen peroxide content of 15 g per litre, another working solution which contains as solvent 70 parts of a hydrocarbon mixture, 15 parts of tris - 2 - ethylhexyl phosphate and 15 parts of N,N - diethyl - N',N' - di - n - butyl urea actually allows an enrichment of only at most 47.6% by weight aqueous hydrogen peroxide.

However, a combination of hydroquinone solvents, i.e. special solvents for alkyl hydroquinones, was not entirely obvious to the expert because the influence of the individual components when used together on the process as a whole cannot be predetermined.

For example, the activity and/or selectivity of the hydrogenation catalyst can vary. The behaviour of the working solution in the extraction stage is not foreseeable. In addition, there is the risk of a negative effect upon the stability of the reaction support and of a possible reduction in the quality of the hydrogen peroxide produced.

Surprisingly, it has now been found that,

contrary to fears, i.e. disturbances in the hydrogenation stage, in the oxidation and extraction stages and a reduction in the quality of the product obtained, it is even possible in the production of hydrogen peroxide by the anthraquinone process to obtain an improvement in the performance of the process as a whole by using as the hydroquinone solvents a mixture of at least two solvents for the alkyl anthrahydroquinones.

Accordingly, the present invention provides a process for the production of hydrogen peroxide by the anthraquinone process, wherein a mixture of at least two hydroquinone solvents is used for dissolving the alkyl anthrahydroquinone, the mixture comprising a tetra-substituted urea with at least one of the following: a phosphoric acid triester, a second tetra-substituted urea, methylcyclohexyl acetate, and diisobutyl carbinol.

Particularly preferred solvent mixtures are mixtures of tetrasubstituted ureas, especially tetraalkyl ureas, with phosphoric acid triesters. Especially preferred mixtures are N,N - diethyl - N',N' - di - n - butyl urea or N,N' - di - n - butyl urea with tris - 2 - ethyl hexyl phosphate.

The quantitative ratio between the individual hydroquinone solvents may vary within wide limits. For example, it is possible very considerably to increase the capacity of a working solution which contains only a single hydroquinone solvent, such as tris - 2 - ethyl hexyl phosphate for example, by adding a tetrasubstituted urea, such as N,N - diethyl - N',N' - di - n - butyl urea.

Since tetra - alkylated ureas generally have more favourable density and viscosity properties than tris - 2 - ethyl hexyl phosphate, the density and viscosity of the solution as a whole are both improved where the phosphate is partly replaced by the urea. The improved selectivity of the hydrogenation stage is clearly reflected in a reduced formation of the extremely undesirable secondary product, alkyl octahydroanthraquinone.

Equally surprising was the quality of the hydrogen peroxide produced in laboratory tests, which is characterised by the carbon content of the product. Under production conditions in a laboratory installation, working solutions with the solvent N,N - diethyl - N',N' - di - n - butyl urea/hydrocarbon mixture gave 40% by weight hydrogen peroxide with a carbon content of approximately 350 ppm, whilst working solutions with the solvent components tris - 2 - ethylhexyl phosphate and hydrocarbons gave hydrogen peroxide of the same concentration with a carbon content of approximately 180 ppm.

With a solvent mixture of hydrocarbons tris - 2 - ethylhexyl phosphate/ N,N - diethyl - N',N' - di - n - butyl urea, it was possible to produce 40% by weight hydrogen peroxide with a carbon content of, again,

tains as solvent mixture 30 parts of tris - 2 - ethylhexyl phosphate and 70 parts of tetramethyl benzene mixture has a maximum practicable production capacity of only 11.5 g per litre of working solution.

The hydrogen peroxide produced in this apparatus with a conventional recycle solution containing only the tetramethyl benzene mixture and tris - 2 - ethylhexyl phosphate as solvent contained the same quantity of carbon, namely 180 ppm.

EXAMPLE 3 75

Three different recycle solutions were subjected to a hydrogenation test at 60°C/6 atms gauge hydrogen pressure in the presence of palladium black. The starting solutions had the following compositions: 80

Solution 1:

Solution 2: 85

50 g of 2 - ethyl anthraquinone in tetramethyl benzene mixture/tris - 2 - ethylhexyl phosphate/N,N - diethyl - N',N' - di - n - butyl urea=70:15:15

Solution 3: 90

50 g of 2 - ethyl anthraquinone in tetra-
methyl benzene mixture/tris - 2 - ethyl-
hexyl phosphate/N,N - diethyl - N',N'-
di - n - butyl urea=70.25 : 5.

After 72 hours, 95

solution 1 had the following quinone composition: 5.34% of 2 - ethyl octahydroanthraquinone and 94.66% of 2 - ethyl tetrahydroquinone;

solution 2: 1.83% of 2 - ethyl octahydro- 100
anthraquinone, 90.17% of 2 - ethyl tetra-
hydroanthraquinone and 8.0% of 2 - ethyl
anthraquinone;

solution 3: 2.67% of 2 - ethyl octahydro-anthraquinone, 88.83% of 2 - ethyl tetrahydroanthraquinone and 8.5% of 2 - ethyl anthraquinone.

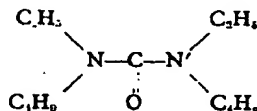
30 The following working solution was tested in a laboratory apparatus adapted to standard working conditions: 85 g of 2 - ethyl anthraquinone, 85 g of 2 - ethyl tetrahydro -
35 anthraquinone in 1 litre of solvent consisting of 75 parts by volume of tetramethyl benzene mixture, 12.5 parts by volume of tris - 2 - ethylhexyl phosphate and 12.5 parts by volume of N,N - diethyl - N',N' - di - n - butyl urea. This composition allowed a production capacity of 12.5 g of hydrogen peroxide per litre of recycle solution.

45 the beginning of the test. In none of the individual stages of the recycle process were there any difficulties attributable to the three-component solvent mixture.

A recycle solution with the following composition was tested in the same apparatus as in Example 1: 100 g of 2 - ethyl anthraquinone, 100 g of 2 - ethyl tetrahydroanthraquinone in 1 litre of solvent consisting of 70 parts by volume of tetramethyl benzene mixture, 15 parts by volume of tris - 2 - ethylhexyl phosphate and 15 parts by volume of N,N' - diethyl - N,N' - di - n - butyl urea. This solution had a production capacity of 15 g of hydrogen peroxide per litre of recycle solution. The 40% by weight hydrogen peroxide produced had a carbon content of 180 ppm.

EXAMPLE 4

The following working solution was tested in a laboratory apparatus adapted to standard working conditions: 85 g of 2 - ethyl anthraquinone, 85 g of 2 - ethyl tetrahydroanthraquinone in 1 litre of solvent consisting of 70 parts by volume of tetramethyl benzene mixture, 15 parts by volume of tris - 2 - ethylhexyl phosphate and 15 parts by volume of N,N' - diethyl - N,N' - di - *n* - butyl - urea



This composition gave a production capacity of 15.5 g of hydrogen peroxide per litre of recycle solution.

- 5 After 700 hours in service, the hydrogenation catalyst still had the same activity as at the beginning of the test. In none of the individual stages of the recycle process were there any difficulties attributable to the three-component solvent mixture.

10 WHAT WE CLAIM IS:—

1. A process for the production of hydrogen peroxide by the anthraquinone process, wherein a mixture of at least two hydroquinone solvents is used for dissolving the alkyl anthrahydroquinone, the mixture comprising a tetrasubstituted urea with at least one of the following: a phosphoric acid triester, a second tetrasubstituted urea, methylcyclohexyl acetate and diisobutyl carbinol.

- 20 2. A process as claimed in Claim 1, wherein a mixture of a tetrasubstituted urea and a phosphoric acid triester is used for dissolving the anthrahydroquinone.

- 25 3. A process as claimed in Claim 1 or 2, wherein a mixture of a tetraalkyl urea and a

phosphoric acid triester is used for dissolving the anthrahydroquinone.

4. A process as claimed in any of Claims 1 to 3, wherein the mixture is of N,N - diethyl - N'—N' - di - n - butyl urea and tris - 2 - ethylhexyl phosphate. 30

5. A process as claimed in any of Claims 1 to 3, wherein the mixture is of N,N' - diethyl - N,N' - di - n - butyl urea and tris - 2 - ethylhexyl phosphate. 35

6. A process for the production of hydrogen peroxide by the anthraquinone process using at least two hydroquinone solvents substantially as described with particular reference to any of the Examples, except Example 3. 40

7. Hydrogen peroxide when produced by a process as claimed in any of Claims 1 to 6.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54, High Holborn,
London, WC1V 6SH,
Agents for the Applicants.